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Mechanisms of Electrophoretic Deposition

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Abstract. There is no single mechanism of electrophoretic deposition (EPD), Just as there are several mechanisms for creating a stable colloidal suspension, there are several mechanisms by which particles can be destabilized to form an adherent deposit at an electrode surface. The goal of this paper is to provide a listing of the mechanisms by which electrophoretic deposition can occur. Several of these mechanisms have already been demonstrated, while others remain speculative. The first step in this process is to provide a clear definition of what exactly EPD is, and, equally important, to clearly distinguish EPD from three other very similar processes: electrostatic coating, electrodeposition, and electrocasting. From this definition a series of logical steps leads to a list of mechanisms by which a stable colloid can be converted to a stable particle compact.

What is Electrophoretic Deposition?

Electrophoretic deposition (EPD) is a particulate forming process. It begins with a dispersed powder material in a solvent and uses an electric field to move the powder particles into a desired arrangement on an electrode surface.

There are four defining characteristics of EPD as it is used here: 1. it begins with particles which are well dispersed and able to move independently in solvent suspension, 2. the particles have a surface charge due to electrochemical equilibrium with the solvent, 3. there is electrophoretic motion of the particles in the bulk of the suspension, and 4. a rigid (finite shear strength) deposition of the particles is formed on the deposition electrode.

What isn't Electrophoretic Deposition?

To clarify the discussions here, it is useful to draw a clear distinction between EPD and three other types of processes which can appear similar, but are still fundamentally different from EPD.

Electrochemical Processes. The first are the electrochemical processes, including: electrodeposition, electroforming, electrocoating, etc. The key word in this case is 'electrochemical'. In these processes a coating is produced by the diffusion and migration of individual ions and molecules to the deposition electrode where they are electrochemically converted to an insoluble form. In the case of electrodeposition and electroforming this reaction is the reduction of metal ions in solution to solid metal. This is a Faradaic process where $n \times 9.65 \times 10^4$ coulombs of current must pass through the cell for each mole of metal deposited, where n is the valence of the metal ions- Another electrochemical process, electrocoating, is best known as the process used for producing the primer coat on automobile bodies. In this case a polymer precursor is deposited by electrochemical polymerization. Electrolysis at the electrode - for example a metal automobile body - produces radicals which drive the reactions. The great advantage of this process is the high resistivity of the formed coating. A set voltage is applied between the auto body and a counter electrode in the bath. When the coating reaches the desired thickness virtually all of the voltage drop between the body and the counter electrode will occur across the polymer coating. Uncoated areas will attract charged polymer precursor to the surface until the desired thickness and voltage drop is reached. This allows the creation of a very uniform coating over a complex shape with many internal channels and spaces. In all of these cases a coating or object is produced that is dense and chemically distinct from the phase in solution.

Electrostatic Processes. The next set of processes that will be distinguished from EPD in this paper are the electrostatic processes: electrostatic precipitation (ESP), electrostatic spraying (ESS), and xerography. Charging in these processes relies on either the high voltage injection of electrons or tribocharging. Chemical reactions are not a factor. A very high resistance fluid in these processes is a requirement to preserve the slight electrostatic charges generated. This means either dry air or non-polar hydrocarbon solvents.

ESP and ESS use sharply pointed corona electrodes to emit electrons at 30 to 100 kV to charge particles in air. ESP is most often used for removing particulates from industrial exhaust gas streams. A precipitator is a large box filled with alternating rows of flat metal sheets and rakes of corona electrodes. A voltage just short of breakdown is applied, and electrons emitted by the electrode tips give particles in the gas stream a negative charge. The particles then move in the electric field to deposit in loose, fluffy layers on the metal sheets.

In electrostatic spraying, a spray gun is used to atomize a powder or paint. In the spray gun is a corona electrode which gives the particles or droplets a negative charge as they exit the spray nozzle. The object to be coated serves as the anode and attracts the charged particles. For liquid paint spraying the advantage of this process is the reduction in overspray that misses the object. In dry powder spraying the electric field is necessary to make the particles stick to the object to be coated. Uncharged particles will not deposit. When the particles are highly resistive they will retain their charge, shielding the object's electric field where they are deposited. This causes additional particles to migrate to and deposit on uncoated surfaces yielding a more even coating than possible with simple spraying or dipping.

Xerography is an electrostatic process that works in the opposite direction. Here it is the substrate that is given the electrostatic charge. A drum with a thin selenium photoconductive coating is given an electrostatic charge by a high voltage corona discharge wire. The drum is then exposed to a pattern of light. Where the drum is illuminated the selenium becomes conductive and the charge is conducted away. The drum then rotates through a dry powder hopper where the powder adheres to areas of the drum that remain charged. The drum then passes over a sheet of paper with an electrode on the other side of the paper. This electrode pulls the particles, which now have their own electrostatic charge, off of the drum and onto the paper. The paper then passes through a fuser where the pigment particles are heated to bond them to the paper.

Electrocasting. The final process in this list is electrocapillary consolidation which will be referred to here as electrocasting. This is a process which is admirably suited to producing large thick section parts as was demonstrated by Ryan et al. [1].

This process begins with a flocced or gelled body of particles in a solvent. Even at extremely low volume fractions particles can floc to form a space spanning structure. This can have a low enough strength that it can appear liquid, and with sufficient shear will behave as a shear thinning particulate suspension. If this structure has a low enough strength an electric field can consolidate these particles to a progressively denser structure. With the proper lubrication between particles this process can achieve very good green densities and uniformities.

There are two key differences between this process and EPD as it is defined here. The first is that the particles are not free to move independently. The consolidation behavior of the gel is dictated by the nature of the particle contacts: the force required to rotate the particles around each other while remaining in contact and the force required to break the contacts. Second the consolidation process is not characterized by electrophoretic migration of particles but by electrocapillary pumping of fluid out of the structure. This can lead to significant hydrostatic pressure gradients through the structure.

Components of EPD

Particle Dispersion. The first step in EPD is the creation of a stable suspension of independent particles. As mentioned above there must be some mechanism to keep the paricles from coming into direct contact where the L-vdW force will hold them together. For the purposes of EPD the particles only need to be "stable" for as long as it takes to go from the end of the dispersing process (sonication, milling etc.) to the end of deposition. Since this can be on the scale of only a few minutes, the easiest form of stabilization is density. If the number density of particles is low enough, only a smalt fraction will come into contact in the bulk during the course of a deposition. The next form of stabilization is electrostatic, where an energy barrier is created which hinders the particles from coming into contact [2]. For the short term stability necessary for EPD this barrier can be between 10 and 15 kT. Finally, there are two major categories of polymeric stabilization. The first is polymer depletion stabilization, which uses a concentration of soluble polymer which is not adsorbed to the particle surfaces. If these polymer chains have a specific ratio of their radius of gyration to the particle radius, then when particles approach there is a repulsive osmotic pressure between them as polymer molecules are squeezed out from the gap between the particles. The other major type of polymeric stabilization requires that a portion of the polymer be adsorbed to the particle and a portion be well dissolved in the solvent. There are many forms of this type of stabilization, categorized by the mechanism of adsorption. A full list can be found in Napper [3]. Some of these stabilization mechanisms are given in Table 1.

Particle Charging. The charging of the particles requires a solvent/electrolyte composition where the adsorption/dissolution equilibria for a positive and negative ion are different. This can take the form of selective dissolution of ions from the particle, selective adsorption of ions from the solvent, and dissociative adsorption of molecules from the solvent followed by preferential desorption of one of the dissociated ions. All of these require a solvent able to support ionic charge

Electrophoretic Migration. How electrochemically charged particles migrate in an electric field is complex topic on its own, and the reader is recommended to references [4] and [5] for a good introduction to the subject. However, it is clear that for there to be electrophoretic migration of particles in the bulk suspension, there must be an electric field.

A solvent with no dissolved ions behaves as a simple dielectric. An applied voltage will result in a linear voltage gradient across the deposition cell as shown in Figure 1. There are fluids that are designed as dielectric insulators which will not support dissolved ions, however, if particles for EPD are to be electrochemically charged, the solvent must, by definition, support dissolved ions.

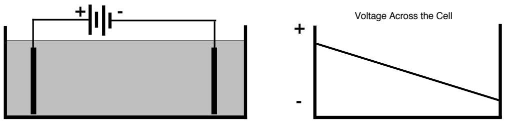

Fig. 1 Voltage across a cell with no dissolved ions

In a solvent with even a tiny concentration of dissolved ions, the picture of the D,C. electric field changes dramatically. If no electrochemical reactions occur at the electrodes then when a voltage is applied, ions will migrate very quickly to oppositely charged electrodes where they will form an electrostatic boundary layer. This electrostatic boundary layer will shield the charge of the electrodes so that the electric field in the bulk suspension will drop effectively to zero. This is shown schematically in Figure 2.

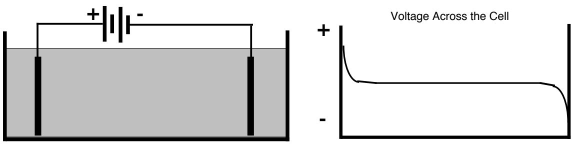

Fig. 2 Schematic of voltage distribution across an electrochemical cell with a concentration of ions but with no electrochemical reactions occurring at the electrodes. Almost the entire voltage drop across the cell will be confined to two very thin layers next to the electrodes.

For there to be an electric field in the bulk of a solution containing even a tiny quantity of dissolved ions there *must* be electrochemical reactions occurring at the electrodes which either produce, consume or change the valence of ions. If particles are migrating electrophoretically in the bulk of the suspension, the ions around them will be migrating even faster. Some reaction must occur to prevent those ions from screening the electric field at the electrode surfaces. This means that electrochemical conduction through the deposition cell is a *necessary* component of EPD.

While these chemical reactions will prevent the creation of charge shielding electrostatic boundary layers at the electrodes, they will do so at the expense of creating electrochemical boundary layers at the electrodes. These are layers where the ionic composition of the suspension can be changed dramatically. Depending on the reactions, the ionic strength can go up or down with accompanying changes in the local electric field. The chemical composition can change dramatically as well. For example, D.C. electrochemical conduction through a neutral $KC1$ salt solution will cause the solution to become acidic at the anode (HCl) and basic at the cathode (KOH).

Deposition of Particles. Particles can be brought to an electrode by electrophoresis, but if there is no difference between the suspension in the bulk and the suspension at the electrode, particles that are stable in the bulk will remain stable at the electrode. As a result there will be no deposition. However, by recognizing the electrochemical changes that occur at the electrode it is clear that there are many ways to change the nature of a suspension so that particles that repel in the bulk can be made to deposit at the electrode.

Creating a list of the possible mechanisms by which EPD can occur is then a simple process of considering each mechanism for stabilizing particles in the bulk and comparing that to a list of changes to the suspension which can be induced at the electrode.

Table 1 contains a list of stabilization mechanisms along with a list of the changes that can be induced at an electrode. Comparing these item by item leads to the list of possible mechanisms of deposition shown in Table 2.

Table 1

Particle Stabilization Mechanisms	Electrode Suspension/Electrochemical Boundary Layer Changes
• Low Number Density	• Increased Particle Density
• Electrostatic	• Electrode Blocking
• Polymer Depletion	• Increased Ionic Concentration
• Homopolymer Adsorption	• Decreased Ionic Concentration
• Terminally Anchored	• Changed Ionic Composition
• Block Co-Polymer	• Increased Electric Field
• Poly-Electrolyte	• Decreased Electric Field

Mechanisms of Deposition

The mechanisms of deposition below are intended to describe the ways that particles come into contact with each other to form a rigid particulate structure. How and if particles come into contact with the deposition electrode surface is an independent subject requiring a different type of analysis. It is possible to form, and the authors have observed, deposits which form at the surface of an electrode but which do not adhere to the electrode surface.

Densification. The fact that the electrode will block the electrophoretic motion of particles means that particles will accumulate there at a higher density than in the bulk. If the particles do not floc in the bulk only because of they rarely come close to each other, they can be brought into contact by suspension densification at the electrode to form a deposit. This mechanism of deposition usually results in very low deposit densities which are difficult to dry without cracking. Also since there is no thickness stabilization mechanism, electroconvection and electric field gradients can lead to very non-uniform deposits.

Direct Electrostatic Force. This again relies on the blocking of the electrophoretic motion of particles by the deposition electrode. In this case the force of the applied electric field on the charged particle is sufficient to overcome the electrostatic repulsion keeping the particles apart. This effect requires very low force gradients between the particles (i.e. thick electrostatic boundary layers) and a high applied voltage, usually several hundred volts/cm [6, 7]. At these high voltages strong electroconvection can lead to patchy, non-uniform depositions on the millimeter scale. Furthermore, the high voltage gradients here interacting with the thick electrostatic boundary layers on the particles can give rise to electroconvective flows around particles and chains of particles which prevent the formation of a dense deposit. Again there is no self leveling effect and particles will deposit by moving along electric field lines or with convective flows.

Electrosedimentary. Hamaker and Verwey [8] proposed that if the electrostatic force on a single particle was not sufficient to cause it to deposit, the force on several layers of particles may be sufficient to cause the innermost layer of particles to deposit in a manner similar to the compaction of gravitational sediments. What was not considered in this simple picture is that the total layer will be charge balanced with an electrochemical charge in the solvent around the particles equal and opposite to the charge on the particle surfaces. This means that there will be a force driving the solvent away from the electrode equal to the attractive force on the particles. There will be a polarization of charge through the layer, reducing the electrophoretic force in the layer. This polarization will lead to unstable hydrostatic pressure gradients, which can cause convection within the layer of particles accumulated but not yet deposited at the electrode. To be most effectively used this mechanism should apply to particles with thin electrostatic boundary layers that can be compacted to a pseudoplastic state to prevent convection in the undeposited layer. On vertical surfaces the suspension should be adjusted to minimize the thickness of the accumulated layer, since gravity can provide enough shear force to cause it to slump or flow off. Given these conditions very good density can be achieved in the as-deposited state.

Ion Depletion Enhanced Electrostatic. In the case where one polarity of ion in solution is consumed at an electrode, the total ionic concentration next to that electrode can drop. As the ionic concentration drops the voltage gradient rises. If convection is suppressed, this process will continue until conduction occurs by unbalanced ions with resulting voltage gradients of millions of volts per meter. These unbalanced charge conduction layers are extremely convectively unstable and are almost never seen in liquid electrolytes. Convective motion at the electrode usually begins before there is any significant voltage rise. However, a powder layer with a high surface area and a rapid surface adsorption equilibria with ions in solution can act as an ionic buffer slowing and stabilizing the formation of an unbalanced charge conduction layer. During constant current deposition voltage gradients of up to several million volts/m can easily arise in this layer [9]. If the particles retain a surface charge this can lead to a very large compaction force. Furthermore, due to the high voltage gradients in the deposited layer, there is a very strong automatic leveling effect.

When it can be achieved, this is an excellent mechanism for producing very uniform thin particulate layers.

Salting Out. The opposite of the ion depletion effect was proposed as a mechanism for the deposition of MgO by Koelmans and Overbeek [10]. In this case the ionic concentration at the deposition electrode goes up, thinning the electrostatic boundary layers on the particles until they became unstable and deposit.

Charge Reduction/Neutralization. Here the change in the ionic composition of the solvent leads to the reduction of stabilizing surface charge on the particle. This could be due to a change in pH at the electrode or the production of a strongly adsorbed ion.

Squeezing Out. In this case, a steady electrophoretic force on the particles can force the polymer from between two particles, allowing them to come into direct contact and form a deposit. This mechanism will, most likely, only be practical with polymer depletion stabilization. There is insufficient information to conclude definitely, but it appears that stabilization in the SiC suspension ofBouyer and Foissy [11] was provided by polymer depletion, therefore, deposition in this case may be a demonstration of this mechanism. Squeezing out the polymer in the case of a weakly adsorbed homopolymer or a terminally anchored polymer at less than full coverage may be possible but will likely be a slow process and may not occur rapidly enough for practical EFD systems.

Bridging Flocculation. If particles are brought into close proximity by electrophoresis, anchor segments on a block co-polymer can desorb from one particle and adsorb to its neighbor creating a polymer bridge to hold the particles together.

Desorption of Neutral/charged Polymer. Changes in the solvent ionic composition can change the surface adsorption equilibrium on the particles so that stabilizing polymer molecules desorb from the particles. This could occur due to a change of particle surface potential or the presence of an ion which outcompetes the polymer for surface adsorption sites. This is a possible mechanism for deposition from suspensions stabilized by polyethyleneimine.

Table 2 Mechanisms of Electrophoretic Deposition

Stabilization Type	Deposition Type	Examples
Low Particle Number Density	Densification	R. Bagwell (Penn State) - BaTi03 (Unpublished)
Electrostatic	Direct Electrostatic	PZT,Ag/Pd [20,21]
“	Electro sedimentary	J. Van Tassel - Alumina
“	Ion Depletion Enhanced	Sarkar and Nicholson -Alumina [24]
“	Salting Out	Overbook-MgO [26]
“	Charge Reduction/ Neutralization	*Unknown*
Polymer Depletion	Squeezing Out	Bouyer&Foissy (?) SiC[27]
Homopolymer	Squeezing Out	*Unknown*
Terminally Anchored at less than full coverage	Squeezing Out	*Unknown*
Block Co-Polymer at less than full coverage	Bridging Floccularion	*Unknown*
Homo-, Terminal-, or Block Polymer	Desorption of Neutral Polymer	*Unknown*
Terminal polymer. Block or Simple Polyelectrolyte	Desorption of Charged Polymer	*Unknown* (Possibly Potyelheneimine)
Polyelectrolyte Electrosteric	Polymer Neutralization	H, Saita (Penn State)- BaTi03 (Unpub-)Polyethyleneimine

Polyelectrolyte Neutralization. Changes in the ionic atmosphere at the electrode can change the ionization of a polyelectrolyte. This can change the solubility of the polyelectrolyte or cause it to desorb from the particle surface. A likely example of this is deposition from suspensions stabilized by polyethyleneimine. A change in effective pH at the cathode could neutralize the positively charged imine groups on the molecule, leading to either desorption from the particles or elimination of an electrostcric stabilizing effect.

Conclusion

These mechanisms of deposition are not exclusive. Two mechanisms could easily occur at the same time. Nor is this a complete picture of electrophoretic deposition. There are many secondary effects beyond just electrophoresis and deposition which occur in almost all real systems. In many cases EPD itself will produce a very low density deposit which is then densified by electrocapillary consolidation. Electroconvective effects acting on several scales can create non-uniform depositions or prevent deposition altogether. Rheology of a drying deposit can determine if it cracks and flakes or forms a high density adherent layer. However, having a specific deposition mechanism as a goal can significantly shorten the suspension design process,

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